Multi-incremental Sampling (MIS) for Metals at the Laboratory

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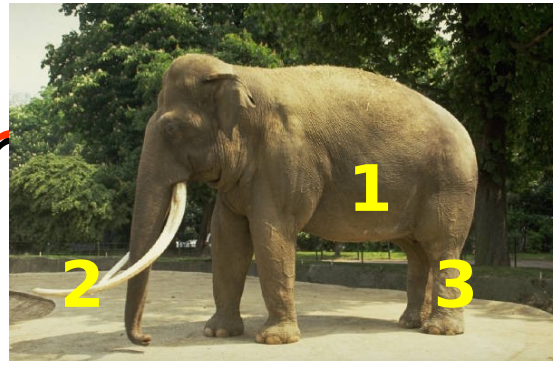
Parable of the Three Blin Men and the Elephant



Three blind men of learning much inclined went to “see” an elephant…

The 1st, falling against its broad side, brawled: *An elephant is very much like a wall !*

The 2nd, feeling it round sharp tuck, exclaimed: *No, its clear an elephant resembles a spear.*

The 3rd, reaching out his hand feeling a knee, cried: *I disagree, an elephant is like the trunk of a tree.*

Discrepant analytical data attributable to sampling design problem.

- ***Population:*** Large herd of elepha

Sample: Each elephant

Sub-sample: Grab (portion of elephant)

Cold Regions Research & Engineering Lab (CRREL):

Grab samples not reproducible because environmental sample is too heterogeneous.

Fundamental Error (FE):

Length (cm) Mass (g)

$$FE\ (\%RSD) = 100\ [\ 22.5\ (\ \mathbf{900}\ )^{3}\ /\ \mathbf{6 \times 10^{6}}\ ]^{½}$$

MIS Approach: Grind, homogenize and collect composite sample

Results: High reproducibility (i.e., good precision):

All three samplers now agree elephant is large amorphous gelatinous creature.

Risk Assessor: Suspects grinding introduced large bias (systematic error) and rejects data as not representative !

Does grinding destroy soil sample integrity for metals?

- MIS-based soil method for metals from Engineer Research and Development Center (ERDC), Vicksburg, MS
  - Deborah R. Felt and Anthony J. Bednar

- Objective: Evaluate precision & bias for un-ground (**UG**) soil versus ground soils using three different grinders: Mortar & pestle (**MP**), roller mill (**RM**), and pulverisette (**PS**).

Figure 1: Roller Mill (RM)
Alumina (85% Al_2O_3) jars coated with
[illegible]thane

Figure 2: Pulverisette (PS)
Agate (SiO_2) grinding bowls & balls.

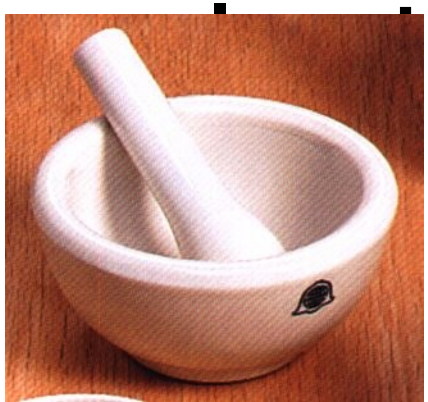


Figure 3: Mortar & Pestle (MP)

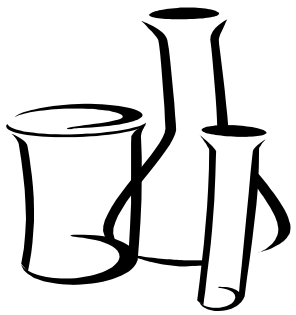
Experimental Design

Treatment	Ottawa Sand	**WES (Ref) Soil**	**GL Soil**
Un-ground (UG)	3	**16**	**16**
Roller mill (RM)	3	**16**	**16**
Pulverisette (PS)	3	**16**	**16**
Mortar & pestle (MP)	3	**16**	**16**
Replicates Total	12	**64**	**64**
Total Samples ICP/MS (6020/3050B)	140 (Excludes batch QC samples)		

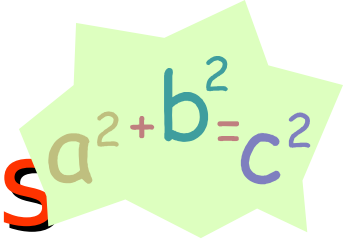
30 Analytes *

Be (Beryllium)
Ti (Titanium)
V (Vanadium)
Cr (Chromium)
Mn (Manganese)
Co (Cobalt)
Ni (Nickel)
Cu (Copper)
Zn (Zinc)
As (Arsenic)
Gd (Gadolinium)
La (Lanthanum)
Nd (Neodymium)
Rb (Rubidium)
Zr (Zirconium)
Sr (Strontium)
Mo (Molybdenum)
Ag (Silver)
Cd (Cadium)
Sn (Tin)
Sb (Antimony)
Ba (Barium)
Tl (Thallium)
Pb (Lead)
U (Uranium)
Ce (Cerium)
Sm (Samarium)
Pr (Praseodymium)
Th (Thorium)
Se (Selenium)

* Target Analyte List (TAL) Metals in bold print

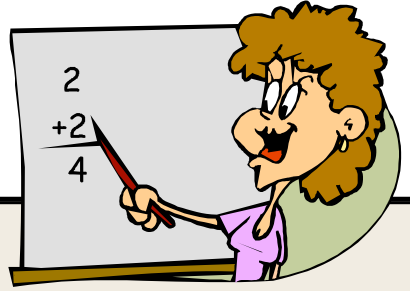


Statistical Evaluations



- Baseline assumptions (null hypotheses):
  - Grinding does not change (e.g., increase) mean/median metals concentrations.
  - Grinding does not change (e.g., decrease) variability (variance).
  - Quantitative comparisons: 95% confidence level (CL) to reject baseline hypotheses.
  - Qualitative comparisons: Box plots

Box Plots

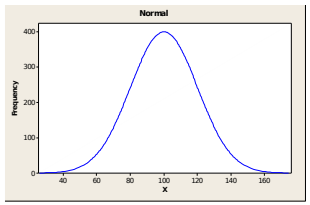


Boxplot of X (Normal), Y (Lognormal)

Concentration

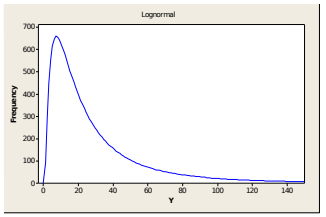
250
200
150
100
50
0

Outlier ⇨ *



Whisker = 1.5 IQR = 2 σ

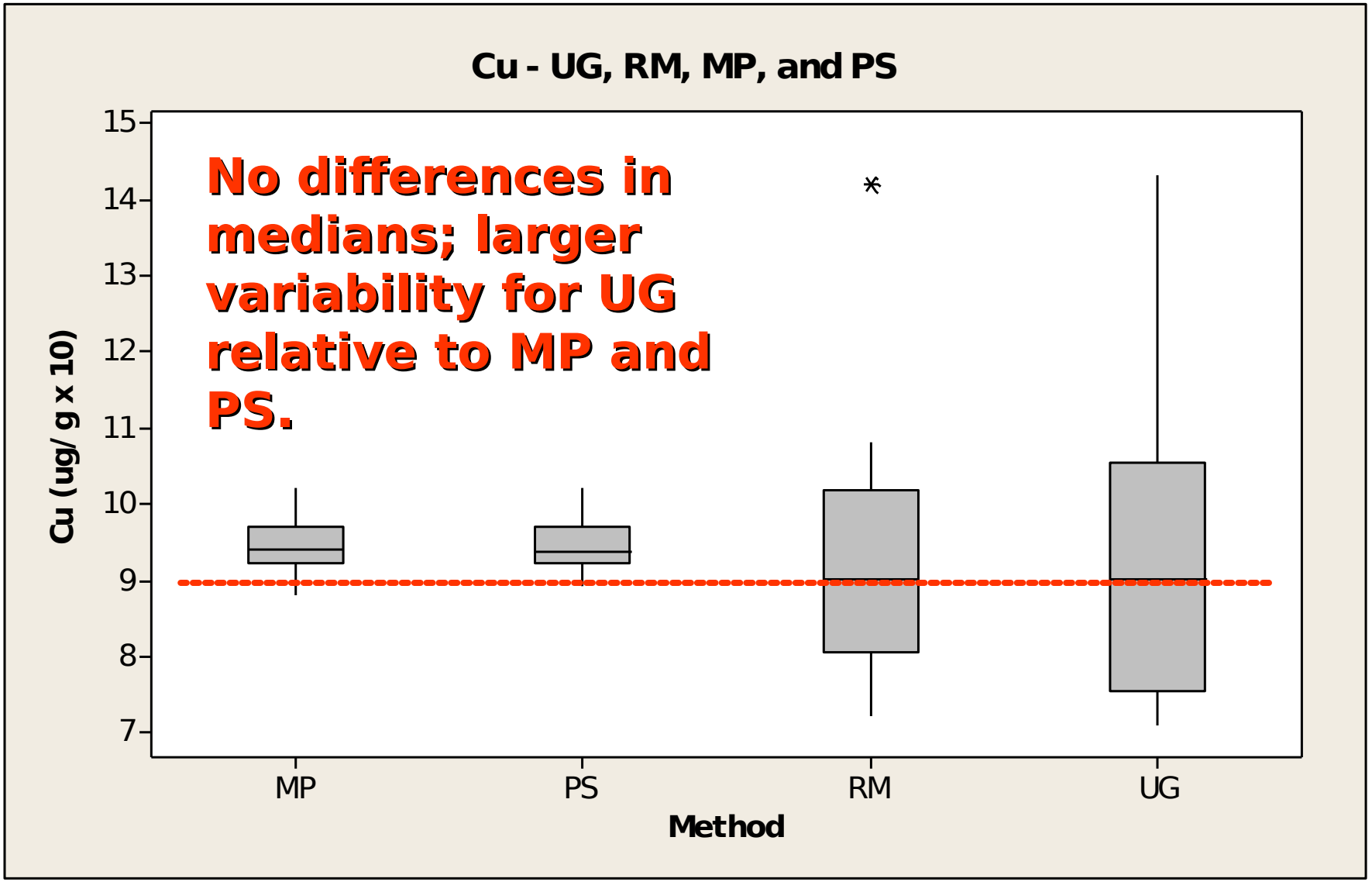
⇦ Median



IQR = 75th – 25th percentile
(Interquartile Range)

X Y

Typical Box Plot, GL Soil

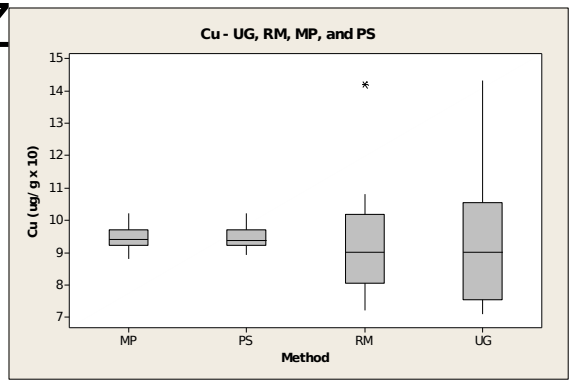


GL Soil, Copper

- Statistical evaluations (using MINITAB):

Kruskal-Wallis Test on Cu (Copper)

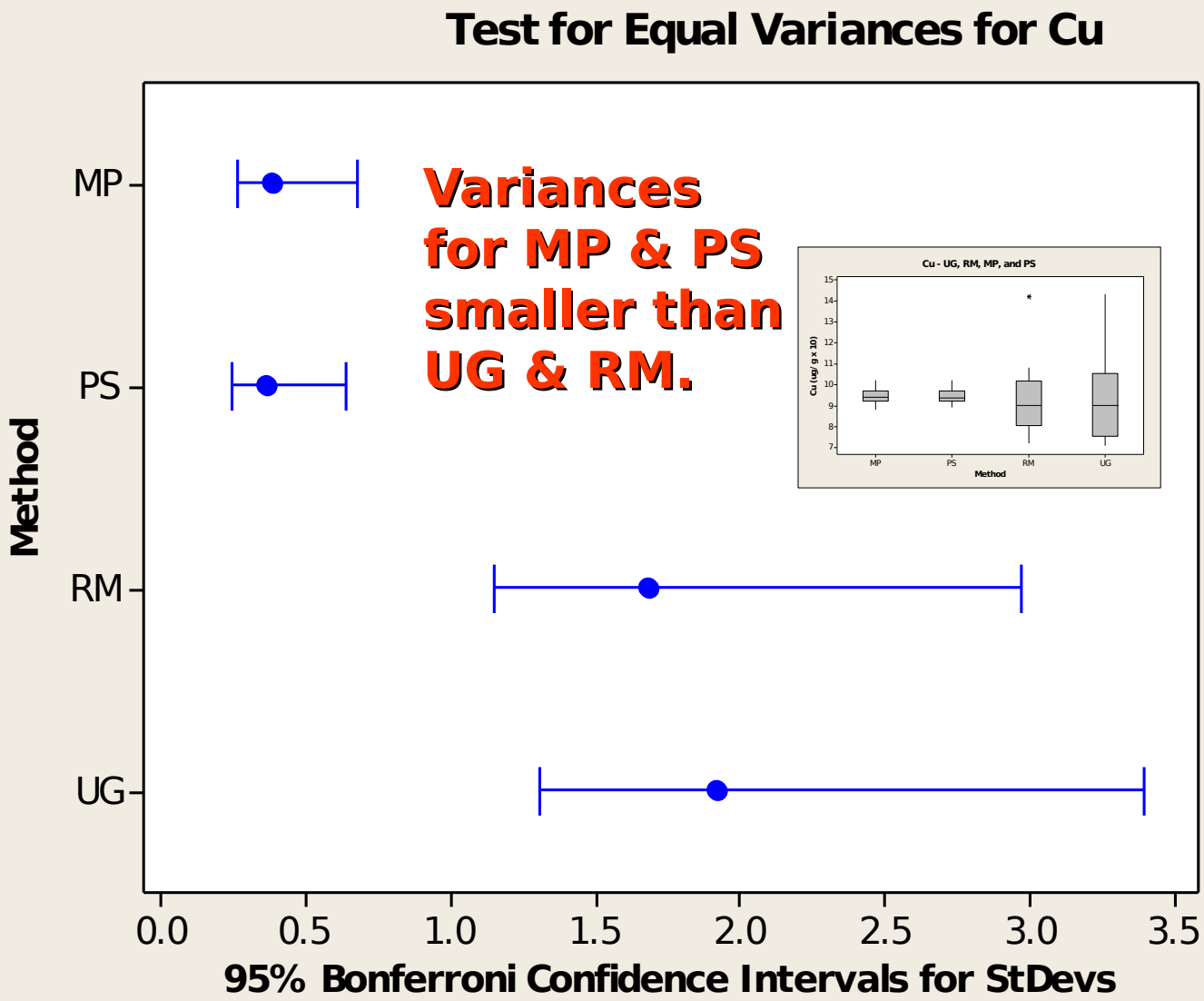
Method	N	**Median**	Ave Rank	Z
MP	16	9.400	37.7	1.29
PS	16	9.350	35.5	0.75
RM	16	9.000	28.8	-0.91
UG	16	9.000	27.9	-1.13
Overall	64		32.5	



H = 3.24 DF = 3 **P = 0.354 (Significant if P < 0.05)**

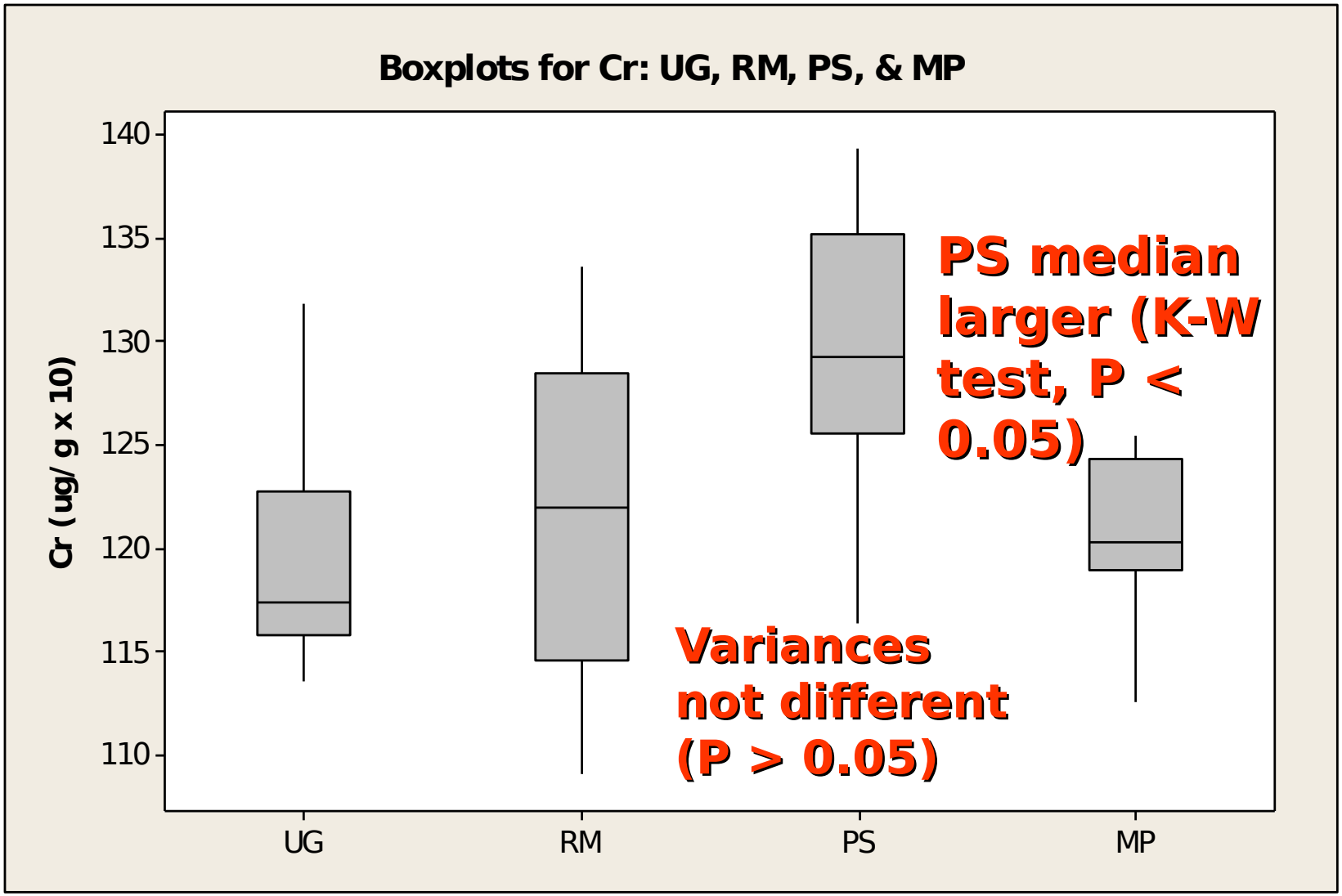
GL Soil, Copper

Cu Copper
Atomic Number: 29
Atomic Mass: 63.55

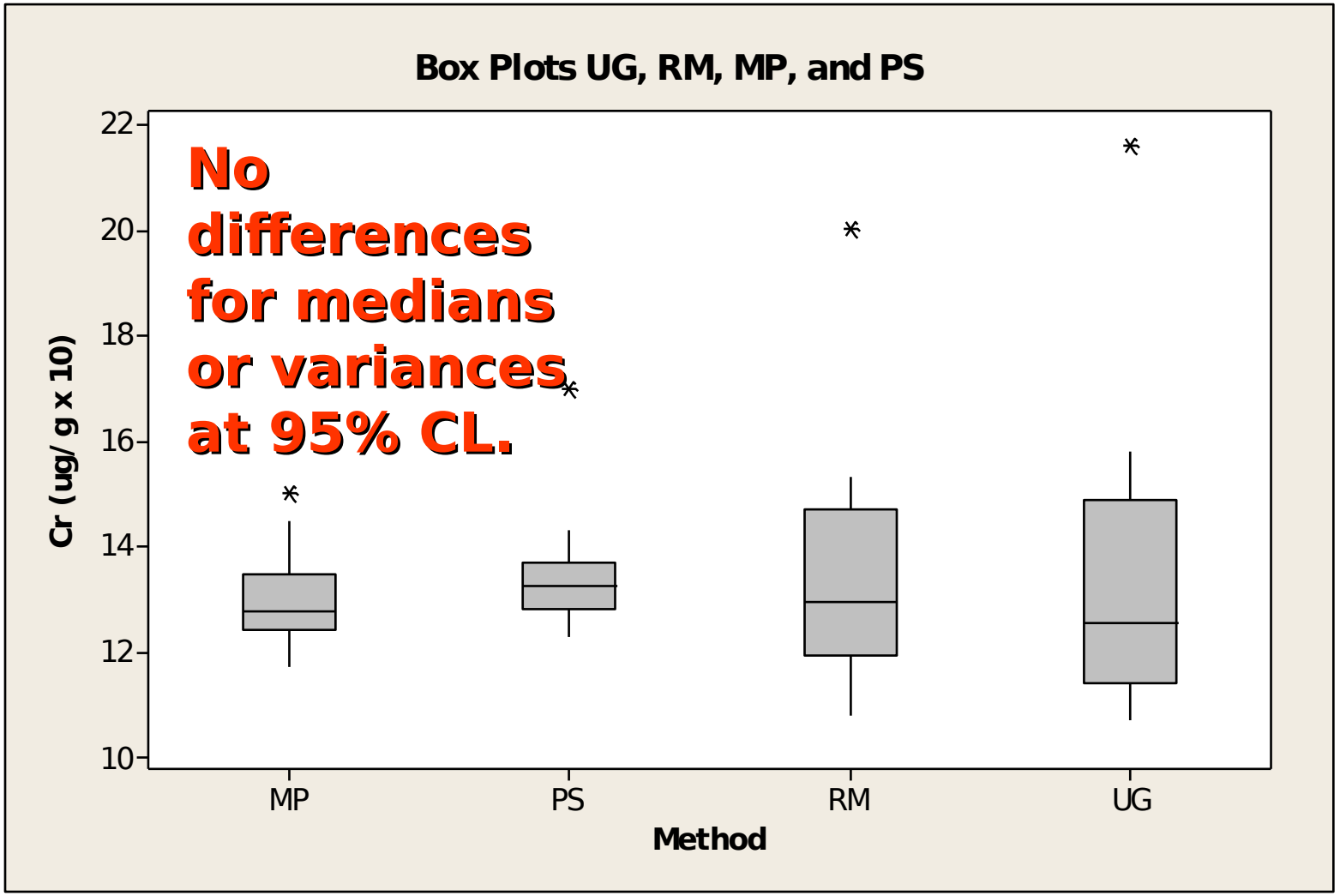


Bartlett's Test	
Test Statistic	54.49
P-Value	0.000
Levene's Test	
Test Statistic	7.06
P-Value	0.000

Chromium, Reference Soil



Chromium, GL Soil



Summary: Reference Soil

- *Overall, grinding had no effect on samples.*
- Most medians not significantly different. Differences usually occurred for only one of three grinding methods, with no obvious pattern.
- However, grinding did not decrease the variances.
  - Soil relatively homogeneous prior to grinding.
  - Desirable for comparisons of the medians (as differences would be attributable to grinding only and not sample heterogeneity).

Some Metals in Reference Soil
(selected randomly)

- No statistical differences for medians:

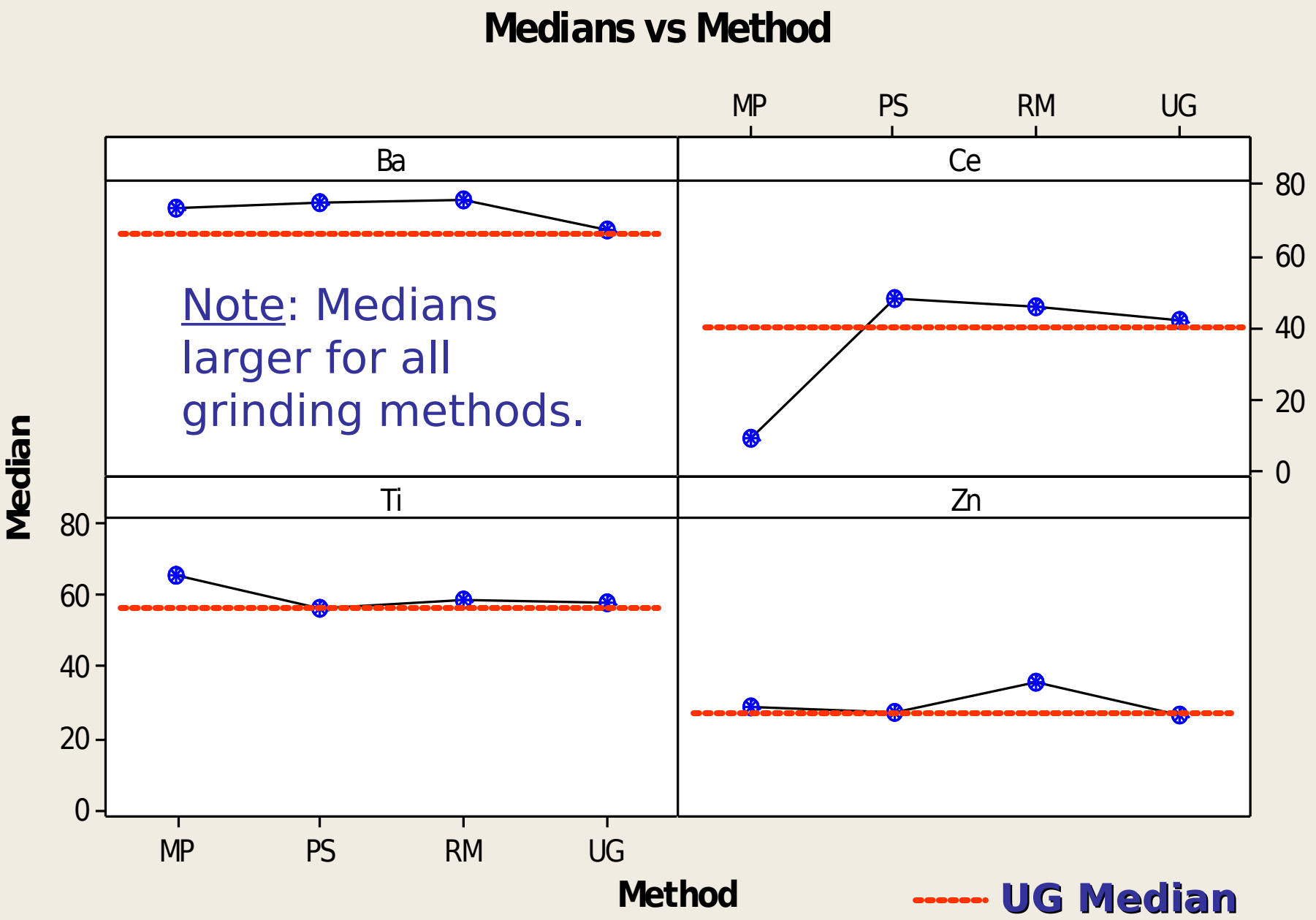
  Pb, Ni, Cu, Cd, As, Co, Tl, Sn

- UG median smaller for one or more grinding methods:

  Zn (RM), Cr (PS), Ti (RM, PS), Ba (PS), Mn (MP), V (PS)

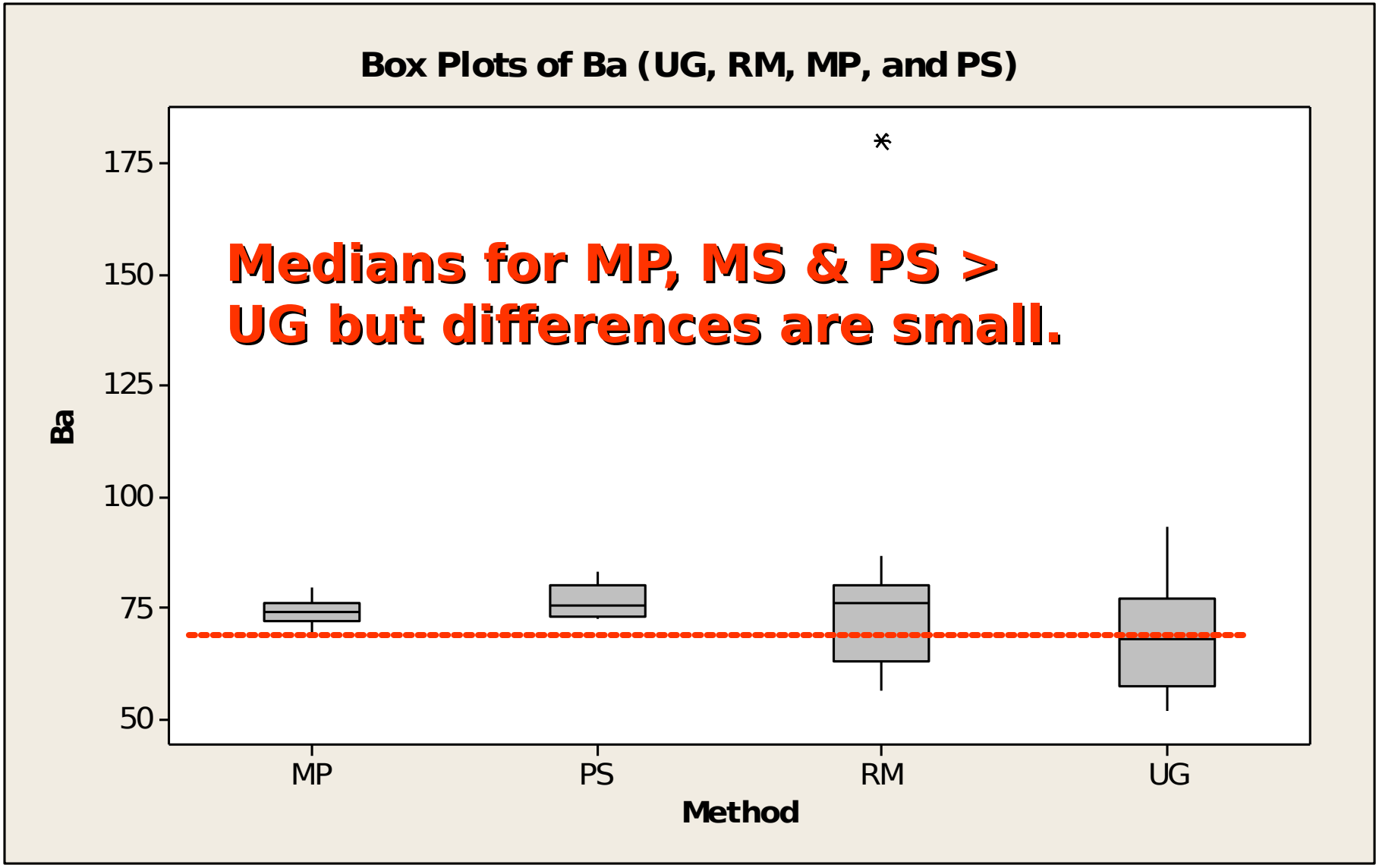
Summary: GL Soil Results

- Overall, variability decreased (with exceptions for RM) and some medians increased.
  - No statistical differences for medians for about 50% of metals.
  - Larger medians for two or more grinding methods for about about 25% of metals; corresponding differences not observed for WES soil with few exceptions (e.g., Zn & Ba).
  - Increases in the medians small; 10% on average.



Select Metals, GL Soil

GL Soil, Barium



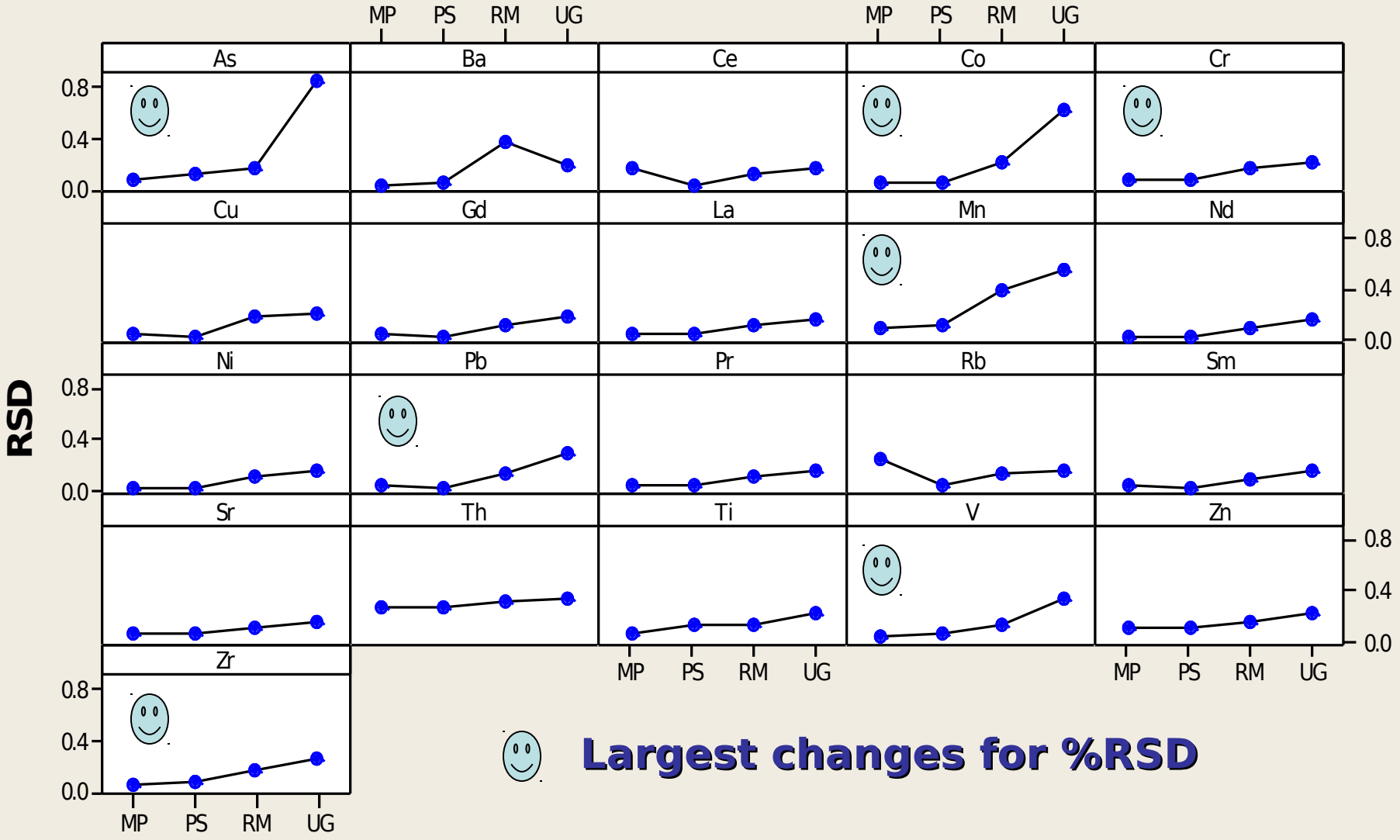
GL Soil Results

- High bias seems to be off-set by improved precision.
  - Relative Standard Deviation:

    RSD = (Standard Deviation)/Median

  - RSD for UG tended to be greater than RSD for grinding methods.

RSD vs Method



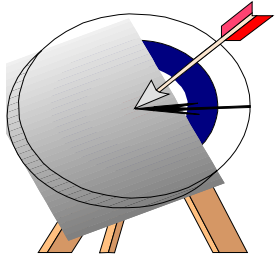
Largest changes for %RSD

Examples, GL Soil

Metal	UG-Median[1]	G-Median[2]	UG-UCL[3]	G-UCL
Ba	68	74 (MP)	74	75 (MP)
As	5.5	6.5 (PS)	8.8	7.0 (PS)

1. UG-Median = Mean for UG
2. G-Median = Median for either RM, MP or PS
3. UCL = 95% upper confidence limit of the (population) mean

Conclusions



- Overall, grinding did not seem to adversely affect the two types of soils evaluated (WES & GL).
- When bias occurred, it was relatively small.
- Grinding (mostly by PS and MP) reduced variability (primarily for GL).
- Study Limitations: Bias & precision depend on soil type. Only one real-world soil (GL) evaluated & did not contain metals as particles.